

PATENT SPECIFICATION

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(19)



(54). PROCESS FOR PREPARING ACID NITRO DYESTUFFS

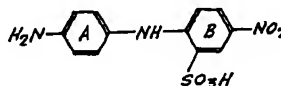
- (71) We, HOECHST AKTIEN-GESELLSCHAFT, a body corporate organised according to the laws of the Federal Republic of Germany, of 6230 Frankfurt/Main 80, Postfach 80 03 20, Federal Republic of Germany, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- The present invention relates to the preparation of acid nitro dyestuffs.
- A proposal has been made in German Patent Specification No. 414,390 to prepare brown dyestuffs by the condensation of benzoquinones with aminonitrodiphenylaminesulphonic acids, the dyestuffs being suitable for dyeing leather and wool. Among these dyestuffs, the condensation of toluquinone (2-methyl-1,4-benzoquinone) and 4-amino-2-methyl-4'-nitrodiphenylamine-2'-sulphonic acid which is known under the name of "Säurelederbraun (Acid Leather Brown) EGB", has an especially great technical importance (cf. Colour Index 3rd edition 1971, C.I. 10415). This dyestuff is prepared by condensing 1 mol of toluquinone with 2 mols of 4-amino-2-methyl-4'-nitrodiphenylamine-2'-sulphonic acid in the presence of sodium carbonate, i.e. in the alkaline range, and in the presence of manganese dioxide (cf. BIOS 1548, page 70). The dyestuff so prepared dyes leather in yellowish medium brown shades.
- British Patent Application No. 4689/74 describes and claims a process for preparing a dyestuff containing at least one acid group and at least one nitro group, which comprises reacting a benzoquinone with an amino-nitrodiphenylamino-sulphonic acid in the presence of manganese dioxide and at a pH below 7, preferably in the range of from 3 to 6. By this process darker and faster dyestuffs may be obtained.
- The present invention provides a process whereby such valuable acid nitro dyestuffs may

also be obtained, which comprises oxidizing an amino-nitro-diphenylamino-sulphonic acid with manganese dioxide in the absence of a benzoquinone at a pH-value of 3 or more. The pH is generally in the range of from 3 to 10, preferably from 3 to 9, and advantageously from 3 to 6 in the acidic range or from 6.5 to 9 in the neutral/alkaline range.

The amino-nitro-diphenylamino-sulphonic acid may be oxidized with manganese dioxide in an aqueous solution at a temperature in the range of from 40° to 100° C, preferably from 50° to 80° C, especially from 60° to 80° C. The dyestuff may then be salted out, suction-filtered and dried.

Suitable amino-nitro-diphenylamino-sulphonic acids include, for example, 4-amino-4'-nitrodiphenylamino-6'-sulphonic acid, 4-amino-2'-nitrodiphenylamino-4'-sulphonic acid, 4-amino-2',4'-dinitrodiphenylamino-6'-sulphonic acid, 4-amino-2',6'-dinitrodiphenylamino-4'-sulphonic acid, 3-amino-4'-nitrodiphenylamino-6'-sulphonic acid; any of these compounds may also be substituted in the benzene nuclei by one or more additional substituents selected from halogen atoms, for example chlorine and bromine atoms, alkyl and alkoxy groups having from 1 to 4 carbon atoms, and carboxy groups.

The process of the invention is especially useful for preparing such dyestuffs which are prepared by oxidation of amino-nitro-diphenylamino-sulphonic acids of the general formula



wherein the benzene rings A and B may be substituted, identically or differently, by one or more additional substituents selected from chlorine atoms, alkyl groups having from 1 to 4 carbon atoms, especially methyl groups, and

alkoxy groups having from 1 to 4 carbon atoms, especially methoxy groups.

The process of the invention avoids the uncomfortable handling of benzoquinones which are physiologically critical and may cause, *inter alia*, injury to the eyes.

The dyestuffs prepared according to the invention dye wool and leather with good fastness properties. Especially on leather they show a good fastness to light, to water and to water drops as well as good fastness properties to fat-liquor (fat emulsions) and organic solvents, especially gasoline, perchloroethylene and carbon tetrachloride. They have a high solubility in water, are fast to formic acid, formaldehyde and alkali, show a very good and even absorption capacity on leather, for example when dyeing in the exhaustion process, and the dyestuffs penetrate leather well and easily. Furthermore, they have a good tanning effect.

With regard to the known dyestuff C.I. 10 415 the dyestuffs show on leather also a darker greenish to bluish shade and have a better fastness to light, to water and water drops as well as a better tanning effect.

The following Examples illustrate the invention. Parts and percentages are by weight unless stated otherwise.

EXAMPLE 1:

307 Parts of 4'-nitro-4-amino-diphenylamino-6'-sulfonic acid were stirred with 1600 parts of water of room temperature (about 20° C). By addition of about 125 parts of 32% sodium hydroxide solution, a pH-value of 8 was obtained. 15 Parts of sodium hydrogen carbonate were added as buffer substance. Then 30 parts of 96% manganese dioxide were introduced. By external heating the temperature was raised to 60° C within about one hour, and the mixture was then maintained at this temperature, initially with cooling because of the reaction heat which was set free. The pH-value began to decrease and then to increase; but it was maintained at 8.0 by addition of sodium hydroxide solution or sulfuric acid. About 1.5 hours after reaching 60° C the pH-value remained constant. After another half an hour the batch temperature was brought to 90° C. To separate the undissolved material the liquid was filtered hot over a suction-filter covered with kieselguhr. To the filtrate and the washing water sodium chloride was added at about 30° C (25 g per 100 ml). The dyestuff precipitated was isolated on a suction-filter or in a filter press, dried at 60° C in a tray drying device and then ground. It dyed leather neutral medium brown.

EXAMPLE 2:

A solution of 343 parts of the sodium salt of 4' - nitro - 4 - amino - 3 - methyl-diphenylamino-6'-sulfonic acid in 1600 parts of water was heated to 55° C and brought

to pH 8.0. Within 10 to 15 minutes 144 parts of 93% manganese dioxide were introduced. The temperature was brought to 60° C and maintained at this level, first by slight external cooling and then by gentle heating. The pH-value was kept at 8.0 by addition of 78% sulfuric acid. When the reaction was finished after about 3 hours and the pH-value remained constant the solution was clarified by suction-filtering over kieselguhr and sodium chloride was added to the filtrate at about 40° C (20 g per 100 ml). The dyestuff precipitated was suction-filtered, dried and ground. It dyed leather slightly reddish medium brown shades.

EXAMPLE 3:

If the reaction was carried out as described in Example 1, but a pH-value of 7.0 was maintained, a dyestuff was obtained which dyed leather brown shades having a slight olive tint.

EXAMPLE 4:

A solution at 75° C of 363.5 parts of 5-chloro - 4' - nitro - 4 - amino - diphenylamino-6'-sulfonic acid in 3000 parts of water was brought to pH 6.5. Within 10 to 15 minutes 120 parts of 93% manganese dioxide were introduced. The pH value was maintained at 6.5 by addition of 78% sulfuric acid and the temperature maintained at 75° C, which required slight cooling.

When the pH value remained constant — which happened after about 3 hours — the reaction was terminated. After clarifying filtration sodium chloride was added to the filtrate at about 50° C (20 g per 100 ml). The dyestuff precipitated was separated, dried and ground. It dyed leather yellowish brown shades.

EXAMPLE 5:

When carrying out the reaction as described in Example 1, but using instead of 4'-nitro-4 - amino - diphenylamino - 6' - sulfonic acid the same amount of 2'-nitro-4-amino-diphenylamino-4'-sulfonic acid, a dyestuff was obtained which dyed leather reddish brown shades.

EXAMPLE 6:

If in Example 2 the sodium salt of 4'-nitro - 4 - amino - 3 - methyl - diphenylamino-6'-sulfonic acid was replaced by 359 parts of the sodium salt of 4'-nitro-4-amino-3-methoxy-diphenylamino-6'-sulfonic acid and the reaction was carried out pH 6.5, a dyestuff was obtained which dyed leather brown shades having an olive tint.

EXAMPLE 7:

321 Parts of 2'-nitro-4-amino-3-methyl-diphenylamino-4'-sulfonic acid were stirred with 1800 parts of water. After heating to 65° C the pH-value was adjusted to 7.0 with

3
concentrated sodium hydroxide solution. Then
120 parts of 93% manganese dioxide were
introduced portionwise within 10 to 15
minutes. The pH-value was maintained at
5 7.0 by dropwise addition of 78% sulfuric
acid. When the reaction was finished after
about three hours, which was indicated by a
constant pH value, the mixture was heated to
10 90° C, suction-filtered over kieselguhr for the
elimination of small amounts of undissolved
contaminations, washed for a short time and
then the filtrate was sprayed in a spray drier
to obtain a dyestuff powder. This powder dyed
leather reddish brown shades.

EXAMPLE 8:

15 307 Parts of 4'-nitro-4-amino-
diphenylamino-6'-sulfonic acid were stirred
with 1500 parts of water. After heating to
65° C the pH-value was adjusted to 3.5 with
20 78% sulfuric acid. Then 125 parts of 93%
manganese dioxide were introduced portion-
wise within 10 to 15 minutes. The pH-value
was maintained at 3.5 by dropwise addition
of 78% sulfuric acid. When the reaction was
25 finished after about 2 hours, which was in-
dicated by a constant pH value, the solution
was suction-filtered over kieselguhr to remove
small amounts of undissolved contaminations,
washed and sodium chloride was then added
30 to the filtrate at about 40° C (20 to 25 g per
100 ml). The dyestuff precipitated was
suction-filtered, dried and ground. It dyed
leather deep olive shades.

EXAMPLE 9:

35 A solution at 70° C of 343 parts of the
sodium salt of 4'-nitro-4-amino-3-methyl-
diphenylamino-6'-sulfonic acid in 3000 parts
of water was adjusted to pH 4.0 with 78%
40 sulfuric acid. 120 Parts of 93% manganese
dioxide were introduced within 10 to 15
minutes. The pH-value was maintained at
4.0 by addition of 78% sulfuric acid. When
the reaction was terminated after about 3
45 hours and the pH value remained constant
the solution was clarified by suction-filtering

over kieselguhr, and sodium chloride was then
added to the filtrate at about 40° C (about
20 g per 100 ml). The dyestuff precipitated
was suction-filtered, dried and ground. It
dyed leather dark brown shades having a
50 violet tint.

EXAMPLE 10:

If the reaction was carried out as described
in Example 8, but a pH value of 6.0 was
maintained, a dyestuff was obtained which
55 dyed leather brown shades having an olive
tint.

EXAMPLE 11:

If the reaction was carried out as described
in Example 8, but 170 parts of manganese
dioxide were used, a dyestuff was obtained
which dyed leather a deep opaque green
60 shade.

EXAMPLE 12:

A solution at 75° C of 363.5 parts of
5 5-chloro-4'-nitro-4-amino-diphenyl-
amino-6'-sulfonic acid and 20 parts of sodium
acetate (as buffer substance) in 3000 parts of
water was adjusted to pH 5.0 with 78% sul-
furic acid. Within 10 to 15 minutes 120 parts
70 of 93% manganese dioxide were introduced.
The pH value was maintained at 5.0 by addi-
tion of 78% sulfuric acid and the temperature
was maintained at 75° C, which required
slight cooling. When the pH value remained
75 constant, which happened after about 3 hours,
the reaction was terminated. After a clarifying
filtration sodium chloride was added to the
filtrate at about 50° C (20 g per 100 ml).
80 The dyestuff precipitated was suction-filtered,
dried and ground. It dyed leather yellowish
brown shades.

EXAMPLES 13 to 23:

The following Table lists further dyestuffs
obtained according to the invention as well
85 as the shades obtained with them on leather.
They may be prepared as described in one of
the Examples 1 to 12 while maintaining the
pH value indicated.

Example No.	Aminonitrodiphenyl-aminosulfonic acid	pH-value	shade
13	4-amino-2'-nitro-diphenyl-amino-4'-sulfonic acid	5.0	green brown
14	4-amino-2'-nitro-diphenyl-amino-4'-sulfonic acid	3.5	green brown
15	4-amino-2',4'-dinitro-diphenylamino-6'-sulfonic acid	5.0	dull brown
16	4-amino-2',6'-dinitro-diphenylamino-4'-sulfonic acid	5.0	reddish brown
17	4-amino-2'-nitro-3-methyl-diphenylamino-4'-sulfonic acid	5.0	medium brown
18	ditto	4.0	medium brown
19	4-amino-5'-chloro-4'-nitro diphenylamino-6'-sulfonic acid	3.0	bluish brown
20	ditto	5.0	dull brown
21	4-amino-4'-nitro-3-methoxy-diphenylamino-6'-sulfonic acid	3.0	olive brown
22	ditto	5.0	olivish brown
23	ditto	6.0	ditto

EXAMPLE 24:

(dyeing of boxcalf leather).

0.025 Part of the dyestuff prepared according to Example 1 was dissolved in 60 parts of water at 55° C. 10 Parts (shaved weight) of calf leather which was tanned with a commercial chrome tanning agent and then neutralized, were introduced into the bath and moved therein at 55° C. After 30 minutes 0.5 part of a commercial synthetic fatliquor and after another 20 minutes 0.025 part of 85% formic acid were added while during the whole time the temperature was maintained at 55° C. After 10 minutes the leather was removed from the dyebath, rinsed and dried.

A leather having a nice neutral medium brown shade was obtained. In the same manner a leather dyeing was obtained with the same quality but in an olive shade when the dyestuff prepared according to Example 8 was used in the dyebath.

EXAMPLE 25:

In the process was carried out as described in Example 24, but instead of the dyestuff used the dyestuff of Example 4 was employed, an evenly dyed leather with a good penetration of the dye and a yellowish brown shade was obtained.

EXAMPLE 26:

(dyeing of suede split).

0.125 Part of the dyestuff prepared according to Example 10 was dissolved in 60 parts of water at 55° C. 10 Parts (dry weight) of chrome tanned skivers were treated for 2 hours in a bath at 50° C consisting of 100 parts of water, 0.1 part by volume of 25% ammonia and 0.08 part of an alkylarylpolglycol ether, then introduced into the dyebath and moved therein. After 45 minutes 1 part of a commercial synthetic fatliquor was added and after another 15 minutes 0.125 part of 85% formic acid, while the dyeing temperature was maintained at 55° C during the whole dyeing period. After 15 minutes the leather was removed from the dyebath, rinsed and dried. An even and nice intense brown dyeing having an olive tint with a good penetration of the dye was obtained.

EXAMPLE 27:

(dyeing of leather of East Indian bastards).

0.075 Part of the dyestuff prepared according to Example 12 was dissolved in 60 parts of water at 60° C. 3 Parts (dry weight) of a vegetable-tanned leather of East Indian bastards were treated for one hour in 50 parts of water at 40° C, introduced into the above-

mentioned dyebath and moved therein. After 45 minutes 0.25 part of a commercial synthetic fatliquor and after 14 minutes 0.075 part of 85% formic acid were added. The temperature of the dyebath was maintained at 60° C. After 15 minutes the leather was removed from the dyebath, rinsed and dried. A nice even dyeing of the leather was obtained in a yellowish brown shade.

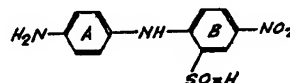
10 WHAT WE CLAIM IS:—

1. A process for preparing a dyestuff containing at least one acid group and at least one nitro group, which comprises oxidizing an amino - nitro - diphenylamino - sulphonic acid with manganese dioxide in the absence of a benzoquinone and at a pH of 3 or above.
2. A process as claimed in claim 1, wherein the pH is in the range of from 3 to 10.
3. A process as claimed in claim 2, wherein the pH is in the range of from 3 to 6.
4. A process as claimed in claim 2, wherein the pH is in the range of from 6.5 to 9.
5. A process as claimed in any one of claims 1 to 4, wherein the reaction is carried out in an aqueous solution at a temperature in the range of from 40° to 100° C.
6. A process as claimed in claim 5, wherein the temperature is in the range of from 50° to 80° C.
7. A process as claimed in claim 6, wherein the temperature is in the range of from 60° to 80° C.
8. A process as claimed in any one of claims 1 to 7, wherein the amino-nitro-diphenylamino-sulphonic acid is selected from 4-amino - 4' - nitrodiphenylamino - 6' - sulphonic acid, 4 - amino - 2' - nitrodiphenylamino - 4' - sulphonic acid, 4 - amino - 2',4' - dinitrodiphenylamino - 6' - sulphonic acid, 4 - amino - 2',6' - dinitrodiphenylamino - 4' - sulphonic acid, or 3 - amino - 4' - nitrodiphenylamino - 6' - sulphonic acid, and corresponding compounds which are substituted in the benzene nuclei by one or more additional substituents selected from halogen

atoms, alkyl groups having from 1 to 4 carbon atoms, alkoxy groups having from 1 to 4 carbon atoms, and carboxy groups.

9. A process as claimed in claim 8, wherein a halogen substituent is a chlorine or bromine atom.

10. A process as claimed in any one of claims 1 to 7, wherein the amino-nitro-diphenylamino-sulphonic acid has the general formula



in which the benzene rings A and B may be substituted, identically or differently, by one or more additional substituents selected from chlorine atoms, alkyl groups having from 1 to 4 carbon atoms, and alkoxy groups having from 1 to 4 carbon atoms.

11. A process as claimed in claim 10, wherein the additional substituents are selected from chlorine atoms and methyl and methoxy groups.

12. A process as claimed in claim 1, conducted substantially as described herein.

13. A process as claimed in claim 1, conducted substantially as described in any one of the Examples.

14. A dyestuff containing at least one acid group and at least one nitro group, whenever prepared by a process as claimed in any one of claims 1 to 13.

15. A process for dyeing leather which comprises treating the leather with a dyestuff as claimed in claim 14.

16. Leather whenever dyed by a process as claimed in claim 15.

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